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(12) Patent:

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(54) RECOVERY PROCESS FOR POLYAMIDES

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ABSTRACT:

CLAIMS: [Show all claims](#)

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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This invention relates to the recovery of synthetic linear polyamides from mixtures of polyamides and extraneous materials.

Polyamides, or nylons, have been used in the production of textiles, and molded and machined articles for some time. Such production has resulted in the accumulation of considerable quantities of waste material, some containing virtually 100% nylon, such as imperfect yarns and imperfectly machined or molded articles. This production has also resulted in the accumulation of considerable quantities of waste material which is highly contaminated with impurities.

These waste materials can be roughly classified into two groups:

1. Waste materials which contain impurities such as dirt, oil, grease, natural fibers and textile treating materials such as delusterants. An example of this type of waste material would be imperfect nylon yarns and textiles, imperfect molded and machined nylon products, textile trimming from a cutting of nylon fabric and scraps of nylon from stamping operations.

2. Waste materials which contain polymeric impurities. This group includes such sources of nylon as nylon-corded automobile, truck, bus and heavy equipment tires, and waste from molders of thermoplastic resins. The nylon would be mixed with other resins such as ABS polymers, polyethylene, polypropylene, polycarbonate, polyformaldehyde, polyacrylates, polystyrene, and natural and synthetic rubber. Included in this group of waste materials are materials which contain a major portion



of polymeric material impurities and a minor portion of polyamide.

Numerous methods of recovering waste nylon have been recorded in the literature. For example, Peterson
5 U. S. Patent 2,348,751 and Stott, et al. Patents 2,592,616 and 2,742,440 describe processes of reclaiming waste nylon. These prior art processes are inadequate in that it is not feasible to employ these processes to recover a nylon scrap contaminated with high molecular weight polymeric
10 impurities and the nylon product of these processes is of substantially inferior quality as compared with virgin nylon. The present invention is not only applicable to the purification of nylon contaminated with high molecular weight polymeric impurities but also results in a nylon of
15 a quality comparable to virgin nylon.

It is an object of the present invention to provide an improved process for the recovery of scrap nylon.

It is a further object of the present invention to provide a process for the recovery of scrap nylon contaminated with high molecular weight polymeric impurities.
20

It is a further object of the present invention to provide a process of recovering polyamide from waste material which contains a major portion of polymeric impurities and a minor portion of polyamide.

25 The polyamide products of the present invention are useful as a substitute for virgin nylon and have particular utility as a nylon molding resin.

The process of the present invention generally comprises the following steps:

30 1. The dissolution of the polyamide mixture with

a high temperature nylon solvent at temperatures between 164°C. and 285°C.

2. The decantation of the hot solution containing the dissolved polyamide from any undissolved impurities.

5 3. The filtration under pressure of the hot solution containing dissolved polyamide.

4. The cooling of the polyamide filtrate to precipitate solid polyamide.

10 5. The separation of the precipitated polyamide from the solvent by filtration step.

6. The drying of the precipitated polyamide to remove unbound solvent.

15 7. Heat treatment of the polyamide at a temperature between 200°C. and 350°C. in vacuo or under inert atmosphere to repolymerize any of the polyamide which may have been degraded.

20 It should be understood that the steps mentioned above are not necessarily distinct operations. A number of the steps may be combined into one actual physical operation.

25 Prior art processes have attempted to purify scrap nylon by heating the scrap nylon to a temperature sufficient to melt the nylon and subsequently filtering the nylon melt under pressure. These processes were inadequate because of the extreme difficulty in filtering the nylon melt. This is the case since molten nylon itself is quite viscous and difficult to filter, and the presence of contaminants compounds the difficulty in filtering the nylon. A method of circumventing this
30 difficulty has been found by rendering the nylon filter-

able as a solution rather than as a melt. The nylon impurity mixture is treated with a suitable nylon solvent which dissolves the nylon. This produces a mixture of solid impurities in a nylon solution. The increased fluidity of the nylon solution as compared with the nylon melt allows the solid impurities to be separated from the nylon by filtration.

10 The dissolution of the waste material by the present invention is carried out by charging the waste material and a suitable high temperature nylon solvent into a high-pressure autoclave, or similar vessel, and heating the contents to a temperature of between 164°C. and 285°C. This dissolves the nylon and renders it filterable as a solution.

20 The selection of the solvent used in this process is of some importance. The volume of mixtures containing large amounts of non-nylon impurities is larger than the volume of the contained nylon. Therefore, the volume of solvent needed to dissolve nylon in mixtures containing large amounts of impurities is also large. Recovery of the nylon by venting off the solvent from the filtrate becomes less desirable economically as the solvent volumes increase. It has now been found that with the selection of a suitable solvent, it is possible to precipitate the nylon by cooling the solution thus avoiding the uneconomic flashing off of large solvent volumes.

30 The use of water as a solvent for nylon has been previously suggested. However such use of water as a solvent for the nylon necessitates considerable degradation (hydrolysis) of the polymer for dissolution to occur. This results in a considerable proportion of the nylon being so far degraded as to be soluble in the solvent, even after cooling of the solution. This difficulty has been circumvented through the use of aqueous solvents better suited to dissolve nylon than pure water, thus allowing dissolution under less stringent conditions. Thus, by employing aqueous solutions of methanol or ethylene glycol, the nylon can be dissolved at temperatures

low enough to avoid excessive hydrolysis of the nylon. Upon cooling the moderately-degraded nylon precipitates from the methanol-water or ethylene glycol-water solution. In this manner, the nylon can be isolated without recourse to flashing off large quantities of solvent.

The solvent should, of course, be a solvent in which the nylon is soluble only at high temperature, that is above 164° C. The selection of a solvent in which nylon is soluble only at high temperatures allows the nylon to be precipitated from the solvent upon cooling. The ultimate recovery of the nylon is thus facilitated.

The solvents for nylon mentioned above are not the only solvents workable in this process. It has been found that lower molecular weight aliphatic alcohols and aqueous solutions of the lower molecular weight aliphatic alcohols in general can serve as nylon solvents capable of dissolving nylon at high temperatures and of precipitating it at lower temperatures. Solvents which irreversibly degrade nylon under the conditions of the process are not practical in this process. For example, acids, which are known to be nylon solvents, react with the polymer at the elevated temperatures of this process to produce a nylon possessing poor physical properties.

Particular solvents that have been found to be useful in the process of the present invention are compounds having the formula $C_n H_{2n+2} O_m$, where n is an integer from 1 to 3 and m is an integer from 1 to 3 but not greater than n . The compounds that are included in this group are methanol, ethanol, ethylene glycol, propanol, trimethylene glycol and glycerol. Aqueous solutions of these solvents and mixtures of the solvents and the aqueous solutions of the mixtures may also be employed. The solvent that is preferred is methanol.

The determination of the particular solvent to be employed in a given instance will depend in some degree on the nature of

the impurities in the waste material. If the impurities are soluble to some extent in alcohols and glycols, it is advantageous to employ an aqueous solution of the alcohol or glycol. The impurities are generally not soluble in water while nylon is soluble in water at elevated temperatures. A substantial amount of the impurities present will therefore remain insoluble and can be separated without difficulty. When aqueous solvents are used however, the degree of degradation (hydrolysis) of the nylon is increased. It therefore becomes necessary to repolymerize the nylon to produce a nylon product with properties comparable to virgin nylon.

Following the dissolution of the nylon, the dissolved nylon is separated from any undissolved impurity by a decantation step. This step allows the major portion of undissolved impurities to be separated from the dissolved nylon without the problem of filter clogging. The decantation step can be carried out by drawing off the filtrate from the autoclave by means of a pump or a siphon or by driving the filtrate out of the autoclave under the vapor pressure of the solvent. It is also possible to transfer the contents of the autoclave to another vessel, allow the insoluble impurities to settle and then decant the nylon containing filtrate. In either case, the temperature of the filtrate should not be allowed to drop below 164°C . Below this temperature, the nylon begins to precipitate.

It is also possible to remove the undissolved impurities from the autoclave rather than decanting the solvent and dissolved nylon from the autoclave. This may be accomplished by charging the waste material into a wire basket and putting the basket into the autoclave. Following the dissolution of the nylon, the basket containing the undissolved impurities may be removed from the autoclave.

The decantation step is not necessary if the impurities present are completely soluble in the solvent. Impurities that

are soluble include delusterants and antioxidants. These impurities can be separated from the nylon because they are soluble in the solvent at a temperature below that which nylon precipitates from the solvent.

10 In order to completely remove undissolved impurities which remain suspended in the solution, it is necessary in some instances to filter the solution through a screen or other suitable filter device. The filtration step should be carried out at a temperature above 164° C. to prevent the nylon from precipitating. This filtration step may be employed in connection with the decanting step. The filtrate would be withdrawn from the autoclave or other vessel and directly forced through the filter element. A pump or the vapor pressure of the solvent in the autoclave may be employed as the driving force to push the filtrate through the filter element.

20 Following this filtration step, the filtrate is transferred to a vessel and allowed to cool or is cooled by refrigeration to precipitate the nylon. The nylon will begin to precipitate when the temperature of the filtrate drops below 164° C. The temperature of the filtrate may be allowed to drop by cooling the filtrate in the atmosphere or by cooling with the aid of mechanical devices such as refrigeration equipment. The preferred method of lowering the temperature is to introduce the filtrate into a large vessel at ambient temperature. This procedure allows the filtrate to cool and precipitate the nylon. The temperature employed to precipitate the nylon may be as low as 50° C, but temperatures this low are not necessary. We have found that substantially all of the nylon will precipitate at 154° C. The preferred temperature range for precipitation is from 154° C. to 163° C. After the nylon has precipitated, it is separated from the solvent by a simple filtration step.

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Following the precipitation of the nylon, the nylon is dried by any suitable means, such as by the use of a circulating air

oven or a vacuum oven. It is necessary in some cases to devolatilize the nylon following the drying. The devolatilization may be performed in any manner suited to the removal of volatile impurities from a polymer at elevated temperatures. At temperatures below the melting point of the polyamide, batch type high temperature driers provided with vents to remove volatile material and an inert gas inlet to blanket the polymer from degrading action of air are suitable. The devolatilization may also be carried out in vacuo rather than in an inert atmosphere. At temperature above the melting point of the polymer, similar machines are suitable including commercial devolatilizing machines, which possess the capability of ready removal of molten polymer from the machine. This devolatilization step besides removing volatile impurities also acts to repolymerize the polymer. This repolymerization of the polymer produces a finished product which possesses excellent physical properties.

The devolatilization or repolymerization is a necessary step when the selected solvent degrades the nylon. The devolatilization is generally carried out at temperatures 200° C. and 350° C., and from 1/2 hour to 3 hours. The time required to repolymerize the nylon will obviously depend on the degree of degradation. If water is present in the solvent system there will be some degree of degradation. The exact degree of degradation is dependent on the period of time the nylon was in contact with the hot solvent. The greater period of time will result in the greater degree of degradation. Generally the period of time necessary for repolymerization is from one-half to three hours. Extending the repolymerization period up to three hours results in a product with more desirable elongation and tensile impact properties. Increasing the repolymerization period to more than three hours continues to improve the properties of the product, but the degree of improvement is diminished.

The following examples, not to be limiting, will serve to illustrate preferred embodiments of the present invention.

Example 1. A mixture of comminuted rubber and nylon, obtained from discarded nylon-corded automobile tires and weighing 5 pounds was charged into an autoclave along with five gallons of 50% (by volume) aqueous methanol, the solids being suspended above the bottom of the vessel by enclosure in a fine mesh screen basket. The temperature was brought to 190°C. and was maintained there for three hours. The autoclave was then cooled and the contents removed. The insoluble materials retained in the suspended basket were discarded. The polyamide and the solvent were found in the bottom of the autoclave and were separated by filtration. The nylon was dried in a vacuum oven in a carbon dioxide atmosphere and then subjected to a 1 mm. vacuum at 260°C. oven temperature for three hours, during which the volatile material was continuously removed from the nylon. The oven was then cooled; the nylon was removed and extruded and chopped into pellets suitable for molding. The intrinsic viscosity of this material in 90% formic acid was 1.0. (Intrinsic viscosity as used herein is defined as in U. S. Patent 2,130,948, except that the 90% formic acid is the solvent employed rather than m-cresol.) The tensile strength of this polyamide was 8180 p.s.i. compared to 7510 p.s.i. for a standard commercial nylon. Both nylons were tested as injection molded, modified dumbbell tensile bars. These and the tensile bars mentioned in subsequent examples were tested after conditioning in a boiling aqueous potassium acetate solution of a specific gravity 1.30 to 1.31, which is equivalent to extensive aging in a controlled atmosphere of 50% relative humidity.

Example 2. A mixture of comminuted rubber and nylon, obtained from discarded nylon-corded automobile tires, and weighing 20 pounds was charged into an autoclave along with 20 gallons of 50% (by volume) aqueous ethylene glycol. The autoclave was brought

to 215°C., during which part of the nylon dissolved. The solution was pumped through a filter and blown out into a cooled receiver. Upon cooling, the nylon precipitated and was filtered off. The solvent was pumped back into the autoclave, and the cycle was repeated several times until no more nylon precipitated from the solution. Upon examination of the insoluble rubber and other residue, it was observed that all nylon had been removed from it. The wet nylon was dried and heat-treated as described in Example 1. After extruding and chopping it, the polyamide was molded into modified dumbbell-type tensile bars. The tensile strength of this material was 8450 p.s.i. compared to 7510 p.s.i. for commercial nylon, and its intrinsic viscosity was 1.0.

Example 3. A mixture of comminuted nylon 6, obtained as scrap from molders of polymeric resins and so contaminated with other polymers such as polyethylene, polystyrene and acetal and with mixed colors and carbon black and weighing two pounds was charged into an autoclave and treated as described in Example 1. After molding into tensile bars, this material possessed the following properties:

Tensile strength 6010 p.s.i., elongation 260%, modulus 1.3×10^5 p.s.i., unnotched Charpy-type impact 39 foot-pounds per inch, tensile impact 184 foot-pounds per inch squared. These values compared to 4910 p.s.i., 320%, 0.66×10^5 p.s.i., 27 foot-pounds per inch, and 192 foot-pounds per square inch respectively for a common, commercial molding grade of nylon 6.

Example 4. A mixture of comminuted nylon 6,6, contaminated with miscellaneous thermoplastic molding resins and with carbon black, and weighing two pounds was charged into an autoclave and treated as described in Example 1. After molding into tensile bars, this recovered nylon possessed the following properties:

Tensile strength 7170 p.s.i., elongation 150%, modulus 1.6×10^5 p.s.i., Charpy-type impact 41 foot-pounds per inch, and tensile

impact 93 foot-pounds per inch squared.

Example 5. This example shows the effect of the heat treatment or repolymerization step on the properties of the product. Samples of virgin nylon and comminuted nylon-corded tires were treated as in Example 1 to the point where the precipitated nylon was recovered. Each sample was divided into three portions and subjected to different heat treatment steps, and the following data obtained:

Recovered Virgin Nylon

Heat Treatment	Tensile p.s.i.	Elongation % at Break	Tensile Impact ft-lbs/in ²
None	7540	80	15
1 hr/260°C/2mm	7700	80	92
3 hrs/260°C/2mm	7750	150	152

Recovered Tire Cord Nylon

Heat Treatment	Tensile p.s.i.	Elongation % at Break	Tensile Impact ft-lbs/in ²
None	7680	50	16
2-1/2 hrs/240°C/2mm	8280	40	38
3 hrs/260°C/2mm	8180	70	182

The above data indicates that the repolymerization step results in improved elongation and tensile-impact properties.

Example 6. The present example shows the recovery of nylon from waste materials containing high molecular weight polymeric impurities. One thousand gram samples containing the impurities in the percentage indicated in the table below were dissolved in the indicated solvent. The mixtures were filtered without decantation, cooled to precipitate the nylon and the nylon was heat-treated for approximately 2 hours, at 260°C. and 2mm vacuum. Test specimens were prepared and tested to show the tabulated properties.

<u>High Molecular Weight Impurity</u>	<u>Solvent (Aqueous Solution)</u>	<u>Tensile p.s.i.</u>	<u>Unnotched Charpy Impact ft-lb/in</u>
17% Acetal	50% glycol	7420	17NB
17% Acetal	50% methanol	7580	38NB
17% Polycarbonate	50% glycol	7600	19(1/4B)
12.5% Polypropylene +			
12.5% Polyethylene +			
12.5 Polystyrene	50% methanol	7650	32NB
10 17% Acrylic	50% methanol	7550	35NB
17% ABS gum plastic	50% methanol	7650	21NB

NB = No sample broken

1/4B = 1 of 4 test samples broken

Example 7. The intrinsic viscosity of commercial nylon molding resin, virgin nylon tire cord, and scrap nylon tire cord hand removed from a scrap tire were determined and compared with the intrinsic viscosity of the recovered nylon of United States Patents 2,742,440 and 2,592,616 and the recovered nylon of the present process.

20 The results are given below:

<u>Type of Nylon</u>	<u>Intrinsic Viscosity</u>	<u>Solvent</u>
Virgin Nylon Cord	1.1	
Commercial Molding Resin	1.2-1.3	
Scrap Tire Cord	0.9-1.0	
Recovered Nylon U.S. Patent 2,742,440	0.66	50% methanol
Recovered Nylon U.S. Patent 2,592,616	0.170	100% methanol
30 Nylon recovered from scrap tire cord, the present process	1.0-1.4	50% methanol

The following Examples 8, 9 and 10 show the suitability of the present process in the treatment of textile type nylon waste materials.

5 Example 8. Virgin textile grade nylon, contaminated with titanium dioxide and textile sizing, was dissolved in 50% methanol at about 200°C. The solution was filtered without decantation, and the nylon was precipitated by cooling. The nylon was dried and heat-treated for three hours at 260°C. The tensile strength of the product was 8020 psi. compared to 7518 psi. for standard commercial grade of nylon 66 molding resin.

15 Example 9. Textile fiber waste containing cotton and rayon as well as nylon was treated as described in Example 8 except for the heat-treatment step which was for 2 hours at 260°C. The product possessed a tensile strength of 7550 psi., elongation over 150%, modulus of 0.69×10^5 psi., notched Izod type impact of 5.1 ft. lbs./in., and an intrinsic viscosity of 1.4.

20 Example 10. Textile nylon 66 waste, scorched and discolored during manufacture was recovered using 100% methanol as a solvent in the process described in Example 8. Heat treatment was conducted for three hours at a temperature of 250°C. The product possessed a tensile strength of 7050 psi., elongation over 100%, and possessed an Izod type impact value of 27, unnotched.

25 Example 11. This example shows the suitability of the present process to recover relatively pure nylon from waste nylon contaminated with a high molecular weight impurity. Molding grade nylon 66 contaminated with 10% by weight of rubber was recovered as described

30

in Example 8 using a heat treatment of 3-1/2 hours at 260°C. The product possessed an intrinsic viscosity of 1.8, a tensile strength of 7580, elongation over 150%, modulus of 2.1×10^5 , and had a notched Izod type impact value of 5.9.

Example 12. This example shows the process of the present process where the nylon material is not unduly degraded by the solvent. Molding grade nylon, contaminated with 10% polystyrene, was dissolved with 100% methanol at 200°C. The polyamide containing the filtrate was decanted and filtered and the nylon precipitated by cooling. The nylon was dried but was not heat-treated. The tensile strength of the product was 9970 psi. and it possessed a melt index of about 7 g./10min., commercial nylon possesses a melt index of 4-8 g./10min. This example show the heat treatment step is not necessary if the nylon is not degraded by the solvent.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of recovering polyamide from a mixture of polyamide and high molecular weight impurities comprising dissolving said mixture in a solvent at a temperature of from 164°C. to 285°C., said solvent being
5 selected from the group consisting of aqueous solutions of compounds having the formula $C_nH_{2n+2}O_m$, where n is an integer from 1 to 3 and m is an integer from 1 to 3 but not greater than n, filtering the polyamide filtrate to separate undissolved impurities, cooling said filtrate
10 to a temperature below 164°C. and above 50°C. to precipitate polyamide from said filtrate, separating said precipitated polyamide from said filtrate, heating the precipitated polyamide to remove unbound solvent, and heat treating said precipitated polyamide in an inert
15 atmosphere to a temperature of from 200°C. to 350°C. for a period of from 1/2 hour to 3 hours.

2. The method of claim 1 in which the solvent is an aqueous solution of methanol.

3. The method of claim 1 in which the solvent is an aqueous solution of ethanol.

4. A method of recovering polyamide from a mixture of polyamide and high molecular weight impurities comprising dissolving said mixture in a solvent at a temperature of from 164°C. to 285°C., said solvent being
5 selected from the group consisting of aqueous solutions of hydroxy compounds having the formula $C_nH_{2n+2}O_m$, where n is an integer from 1 to 3 and m is an integer from 1 to

3 but not greater than n, filtering the polyamide filtrate
to separate undissolved impurities, cooling said filtrate
10 to a temperature below 164°C . and above 50°C . to pre-
cipitate polyamide from said filtrate, separating said
precipitated polyamide from said filtrate, drying the
precipitated polyamide to remove unbound solvent, and heat
treating the precipitated polyamide at a temperature be-
15 tween 200° and 350°C . in vacuo for a period of from $1/2$
hour to 3 hours.

5. The method of claim 4 in which the solvent
is an aqueous solution of methanol.

6. The method of claim 4 in which the solvent
is an aqueous solution of ethanol.